B96-33

Attachment 2

BASF CORPORATION
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Study Title:

437800-01

Method for Determination of Residues of Pyridaben in Apple and Apple Processed Commodities by Gas Chromatography

Study No. 93186

Method No. D9312

Data Requirement:

Guideline 171-4(c) Analytical Method

Author:

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Study Completion Date:

April 1994

Testing/Performing Laboratory:

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BASF Registration Document No._____

This report consists of 60 pages.

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PR 86-5 DATA CONFIDENTIALITY CLAIM

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA 10 (d) (1) (A), (B) or (C)

Company BASF Corporation, Agricultural Products

Company Agent Rodney C Akers Date Aug. 15, 1995

Title Registration Scientist Signature Rodney C. Akers

GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

This study meets the requirements for 40 CAR Part 160, except the section on method specificity (Interferences, Section 3.4). Not all the compounds recieved from the EPA Pesticide Repository, from Ultra Scientific, and from Chem Service, Inc. have complete documentation for characterization and purity analysis. The documentation received is the best available.

Submitter: Rodney C. Aken 8-15-95

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Method for Determination of Residues of Pyridaben in Apple and Apple Processed Commodities by Gas Chromatography

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Method No. D9312 **Report Date: April 1994**

ABSTRACT:

Analytical Method Number D9312 was developed to determine the residues of Pyridaben (BAS 300 I) in apple and apple processed commodities. Method development and validation were carried out at BASF Corporation, Research Triangle Park, N.C., using representative control apple and apple processed commodities from residue processing studies. Pyridaben is extracted from the apple matrices by using an acetone/water solution (8.2 v/v). Extracts are purified by C_{18} solid phase extraction (SPE). A gas chromatography system with electron capture detection is used for the final determination. This study has shown that Analytical Method Number D9312 is suitable for measuring residues of pyridaben in apple and apple processed commodities down to a quantitation limit of 0.05 ppm. The average recoveries for all matrices were 93±11% (n=71).

Experimental Dates:
Start: November 23, 1993
Termination: December 31, 1993

STATEMENT OF THE QUALITY ASSURANCE UNIT

Method Number: D9312
BASF Study Number: 93186

Study Initiation Date: November 23, 1993

The quality assurance unit of the testing facility at the ARC has audited the protocol, the analytical portion including the raw data, and the report for this study and reported its findings to the study director and to management.

Date of Audit	Report to Study Director and to Management
11/12/93	11/12/93
11/29/93	11/29/93
12/02/93	12/02/93
3/31/94	3/31/94
4/14/94	4/14/94

Signature of QAU

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1 Introduction and Summary

1 1 Scope and Source of the Method

1.1.1 Scope

Pyridaben (BAS 300 I) is an acaricide developed by NISSAN Chemical Industries for mite control in fruit crops. This report describes the analytical procedure developed by BASF to determine residues of pyridaben in apples and its processed commodities (dry pomace, wet pomace and juice). A similar method was developed at BASF to analyze oranges and orange process fractions (Reference 1).

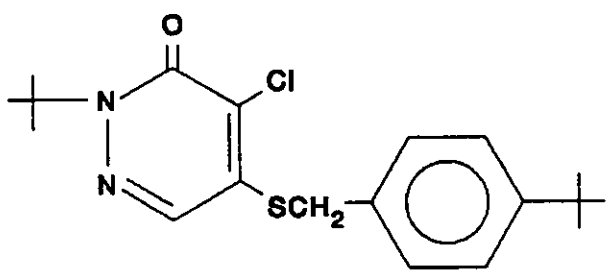
1.1.2 Source

This method was developed at the BASF Agricultural Research Center in Research Triangle Park, North Carolina.

1.2 Substance

Common Name·	Pyridaben
BAS Number:	BAS 300 I
Chemical Name·	4-chloro-2-(1,1-dimethylethyl)-5-[[[4-(1,1)-dimethyl-ethyl)phenyl] methyl]thio]-3(2H)-pyridazinone
CAS Name:	96489-71-3

Structural Formula:



Empirical Formula.	$C_{19}H_{25}ClN_2OS$
Molecular Weight:	364.9 g/mole
Melting point:	111-112°C
Boiling point:	NA
Appearance:	White Crystalline Solid

Solubility· (g/100 mL solvent at 20°C)

Acetone	46
Acetonitrile	6.9
Dichloromethane	15.3
Ethanol	5.7
n-Hexane	1.0
Water	1.2×10^{-6}

1 3 Standard and Standard Stability

Purity	99.5% Lot# 129S8604 Supplied by NISSAN Chemical Industries Agrochemical Division Tokyo, Japan

The standard when in solution (acetonitrile) is stable for at least 4 weeks when kept in a refrigerator at 4°C in the dark (Reference 2).

1.4 Principle of the Method

Pyridaben is extracted from the homogenized or well mixed matrices using an acetone/water solution (8:2, v/v). After filtration to remove solid material, an aliquot is mixed with water and applied to a mini-C_{18} column. The eluent from the column is evaporated and the sample is dissolved in toluene for GC-ECD determination of pyridaben.

2. MATERIALS

2.1 Equipment-Suggested Sizes/Manufacturers

Flat-bottom flask, 24/40	50, 125, 250 mL
Buchner funnel	11 cm diameter
Separatory funnel	125 mL, 250 mL
Funnel, long stem	75 mm diameter, 150 mm stem
Funnel, short stem	75 mm diameter, 75 mm stem
Volumetric flask	10-500 mL
Volumetric pipette	0.5-10 mL
Filter flask	500 mL
Glass SPE column 8 mL	Doe & Ingalls, Item No. 7328-06
Filter paper	Whatman 1PS, No. 4 and 5 (11 and 24 cm)
Pasteur pipets, disposable	23 cm long
Autosampler vials 1 5 mL	Sun Brokers, Inc. or equivalent
Autosampler snap caps 11 mm	Sun Brokers, Inc. or equivalent
Glass wool	e.g. sterile
Vortex mixer	Fisher Scientific or equivalent
Ultrasonic bath	Branson 1200 or equivalent
Nitrogen stream evaporator	N-Evap Organomation Associates, Inc. or equivalent
Stirring hot plate	Corning or equivalent
Balance (with at least one-tenth of a gram capability	Mettler or equivalent
Polytron homogenizer	Brinkmann Instruments
SPE manifold	Supelco, Inc or equivalent
Rotary evaporator	Buchi or equivalent
Water bath	Buchi or equivalent
Vacuum system for rotavap	Elnik Systems IPM Inc

2.2 Reagents and Chemicals - Source/Preparation

Reagents and Chemicals	Source/Preparation
Acetone	Distilled, high purity (Burdick & Jackson)
Ultra pure water (18 Megaohm•cm resistivity)	Millipore water purification system or equivalent
Dichloromethane (DCM)	Distilled, high purity (Burdick & Jackson)
Methanol	Distilled, high purity (Burdick & Jackson)
Hexane	Distilled, high purity (Burdick & Jackson)
C_{18} Silica Gel (40-60 μm)	Fisher Cat.# 10162 or J.T. Baker

Note: Reagents and chemicals equivalent to the above may be used.

2.2.1 Standard Solutions for Fortifications

Pyridaben (BAS 300 I): the recommended concentrations are 1000, 100, 50, and 1 μg/mL in acetonitrile. Standard solutions should be stored in amber glass bottles in a refrigerator (approximately 4°C).

Prepare a 1000 μg/mL (1 mg/mL) BAS 300 I stock solution by transferring an appropriate amount into a volumetric flask. Dissolve with acetonitrile and dilute to the mark. For example to prepare a 25 mL stock solution, dissolve 25 mg of BAS 300 I in a 25 mL volumetric flask with acetonitrile. Dilute to the mark with acetonitrile. Stock solutions (1 mg/mL) were made fresh every three months. Dilutions of the stock solution were made monthly.

Prepare a 100.0 μg/mL BAS 300 I standard solution by transferring an appropriate amount of the 1000 μg/mL stock solution with a volumetric pipet to a volumetric flask (typically 5 mL of the 1000 μg/mL stock solution into a 50 mL volumetric flask). Dilute to the mark with acetonitrile.

Prepare 50.0 μg/mL and 1 μg/mL BAS 300 I standard solutions by making appropriate dilutions or sequential serial dilutions of the 100 μg/mL standard solution and diluting with acetonitrile. Other concentrations may be used as appropriate.

2.2.2 Standard Solutions for GC Analysis

Pyridaben (BAS 300 I): The recommended concentrations are 500, 100 50, 25, 12.5 and 5 ng/mL in toluene. Standard solutions should be stored in amber glass bottles in a refrigerator (approximately 4°C).

2.2.2 Standard Solutions for GC Analysis (continued)

Prepare a 500 ng/mL BAS 300 I standard solution by transferring an appropriate amount of the 50 µg/mL standard solution in toluene (see Section 2.2.1) with a volumetric pipet to a volumetric flask (typically 1 0 mL of the 50 µg/mL standard solution into a 100 mL volumetric flask). Dilute to the mark with toluene.

Prepare 100 ng/mL, 50 ng/mL, 100 ng/mL, 12.5 ng/mL and 5 ng/mL standard solutions by making appropriate dilutions of the 500 ng/mL standard solution and diluting with toluene. Other concentrations may be used as appropriate.

3 Analytical Procedure

The following procedure is for whole apple, wet pomace, dry pomace and apple juice. A flow chart for the analytical method is presented in Figure 1.

3.1 Preparation of Samples

Homogenize apple and apple processed commodities samples thoroughly before subsampling and weighing (shake the juice well before removing an aliquot). Remove any extraneous material. Depending on the sample consistency, the samples may be homogenized manually (i.e. juice) or mechanically. Whole apples were homogenized first with a Hobart Chopper followed by a Meat Grinder. The wet pomace was homogenized with a Meat Grinder, while dry pomace was homogenized in an Urschel Comitrol with dry ice. The dry ice was allowed to sublime in the freezer. Samples were stored in suitable containers with bar coded labels containing the same information as the original label.

3.2 Method for Whole Apple, Wet Pomace, Dry Pomace, and Apple Juice

3.2.1 Extraction

a. Weigh 25 g (±0.2 g) of the homogenized apple matrix sample (10 g in case of dry pomace) into a 250 mL glass bottle or container. Fortify controls to be used as procedural recovery samples with appropriate concentrations of the pyridaben standard (e.g. for 0.05 ppm, add 1.25 µg/mL to 25 gram of apple).
b. Add 100 mL of acetone/water (8.2 v/v) to the glass bottle and macerate the sample for 2-3 minutes with a polytron.

Note: For apple juice, do not use the polytron. Add 200 mL of 80% acetone/water to 25 g apple juice, shake well and follow the procedure, step 3.2.1.d

c. Rinse the polytron blade with acetone/water (8/2 v/v). Collect the rinses in the glass bottle.

d. Vacuum filter the slurry through a Buchner funnel containing 1 sheet each of Whatman No. 4 and 5 filter paper into a 500 mL filter flask. Use 80% acetone/water from a squeeze bottle to rinse the filter materials (stop the vacuum during the wash). Adjust to an appropriate volume (e.g 250 mL or 500 mL), by adding acetone/water (8/2 v/v) to the extract.

Note: Use one sheet of filter paper (No. 5) to cover the base of the Buchner funnel and a second sheet of filter paper (No. 4, larger than the diameter of the funnel) pressed down inside the funnel to prevent the small particles from clogging the first filter paper.

e. Quantitatively remove 2% (e.g. take 10 mL from 500 mL) of the extract (4% in case of dry pomace) from the previous step and place into a 50 mL tube or 125 mL, 24/40 standard flat-bottom flask. Date, label and store the remaining extract. Add an equivalent amount of water to the extract and mix the contents on a vortex mixer.

Note: Depending on the sensitivity of the GC detector, different aliquot sizes may be used as needed.

3.2.2 C_{18} Solid Phase Extraction

A mini-C_{18} column clean-up step will be used before the final GC determination. The following procedure is used for the C_{18} cleanup:

3.2.2.1 Column Preparation

a) Weigh out 1.0 gram of C_{18}-silica gel (40-60 μm partial size). Transfer the sorbent into an 8 mL glass column with a teflon frit (Doe & Ingells, Durham, NC) at the bottom and place a glass wool plug (about 50 mg; the weight is not crucial, but also should not be excessive) at the top of the C_{18} silica gel

b) Use an SPE vacuum manifold (aspirator) to perform all the steps for C_{18} SPE column. A vacuum reading of 4-6 inches Hg has been adequate (solvent flow rate is 6-8 mL/min).

Note: The flow rate may change depending on the type of matrix. In this case keep the vacuum reading between 4 to 6 inches Hg.

3.2.2.1 Column Preparation (continued)

c) Condition the mini-C_{18} column by passing 20 mL of methanol followed by 20 mL of 40% acetone/water through, without allowing the column to go dry.

Note: Prepacked C_{18} SPE columns from J.T. Baker were tried, but the matrix sample clogged the top frit and stopped the flow of the solvent.

3.2.2.2 Sample Load

Transfer the extract solution (e.g 20 mL or 40 mL in case of dry pomace) to the conditioned mini-C_{18} column. Collect the eluant in a waste container (e.g. 200 mL beaker).

3.2.2.3 Column Wash

Wash the container with 80 mL of 60% methanol/water and swirl to dissolve any residues left from the previous step. Add this wash to the column. Collect the eluant in the waste container.

3.2.2.4 Analyte Elution

a. Elute the pyridaben with 40 mL of 80% methanol/water (v/v). The ratio of methanol to water may change depending on the lot number of the C_{18} silica gel. Elution profiles must be established for each lot of C_{18} silica gel). Collect the elution solvent in a 50 mL or 125 mL flat bottom flask.

b. Evaporate the eluant on a rotary evaporator with the water bath maintained at a maximum of 50-65°C to just dryness. Remove traces of the solvent using a low stream of N_2.

Note: During the evaporation step, if the sample is foaming, add 10 mL of toluene and evaporate to dryness. Repeat this step if necessary.

3.2.2.5 Preparation for Final Determination by Gas Chromatography

Dissolve the samples in an appropriate volume of toluene for final GC determination, sonicate and vortex for 30 seconds. The control and 0.05 ppm fortification samples should be diluted to the same volume (typically 2 mL). Analyze the samples by gas chromatography with electron capture detection (GC-ECD).

3 3 Instrumentation

Gas Chromatograph:	Hewlett Packard 5890 Series II	
Detector:	^{63}Ni-ECD	
Capillary Column:	J & W Scientific	
	Column 1	Column 2
Length:	15 m	30 m
Internal Diameter:	0.32 mm	0.32 mm
Stationary Phase:	DB-5	DB-17
Film Thickness:	1.0 µm	0.5 µm
Injection Temperature:	250°C	
Oven Temperature:		
For column 1:	130°C for 0.5 min, ramp at 30°C/min to 230°C and hold for 7 minutes, ramp at 30°C/min to 275°C and hold for 6 minutes.	
For column 2:	150°C for 1 min, ramp at 25°C/min to 275°C and hold for 16 minutes	
Detector Temperature:	300°C	
Carrier Gas:	Helium	
Injection Volume:	2 µL	
Autosampler:	Hewlett Packard 7673	
Retention Time:		
For column 1:	10 minutes	
For column 2:	13 minutes	

Notes: The retention time may vary from one column to the other and also with the length of the column which will change when the ends of the column are cut for routine maintenance.

Other GC instruments with similar performance can also be used, after GC conditions have been adjusted, if necessary. The GC parameters may be varied depending on required peak resolution or specific separation problems.

3.4 Interferences

If interfering peak(s) from the matrix occur in the chromatogram, alter the GC oven program or column flow rate. Other types of GC columns may be used. GC-MSD can be used as a confirmatory technique. See Section 3.5.

3 4.1 Sample Matrices

None observed to date.

3.4.2 Other Sources

Other Pesticides:

In order to determine the specificity for this analytical method, the compounds registered for use on pome fruits and citrus fruits were examined. Of the 125 compounds which have tolerances established (Table IV), 30 could be eliminated because they were incompatible with GC analysis. These were mainly salts and inorganic compounds. An additional 11 compounds were unavailable from standard sources (the EPA Pesticide Repository, Ultra Scientific, ChemService, Inc.). Standard solutions (500 ng/mL) of the remaining 84 compounds were prepared and injected into the GC-ECD under conditions established for the determination of pyridaben. Of these, only three compounds were detected within the retention time window (9.47 ± 0.15 minutes) for pyridaben: permethrin, thiophanate and azinphosmethyl. These three compounds were then subjected to the cleanup steps (silica and C_{18} chromatography) and the eluates reinjected. None of the three was detected. Therefore, the method is specific for the analysis of pyridaben in pome fruits (and citrus fruits).

Solvents:	None observed to date.
Lab Ware:	None observed to date.

3.5 Confirmatory Techniques

A different column, DB-17 (30 m, 0.32 mm, 0.5 μm), can be used as an alternative column for pyridaben residue analysis. A thermionic specific detector (TSD) can be used as an alternative detector, but its sensitivity is approximately 1/10 that of the ECD. GC-MSD was used as a positive confirmatory technique.

3.5.1 Description of Equipment

Gas Chromatography:	Hewlett Packard 5890 Series II
Detector:	Hewlett Packard 5970 mass selective detector. The instrument is manually tuned once a week for maximum sensitivity (for ion m/z 219) using perfluorotributylamine. Detection by selected ion monitoring (SIM) at m/z 365 ($M^{+\bullet}$) and 309 ($M^{+\bullet}$-C_4H_7). The dwell time is one second.

3.5.1 Description of Equipment (contiued)

Capillary Column:	J & W Scientific
Length:	30 m
Internal Diameter:	0.32 mm
Stationery Phase:	DB-17 (50% diphenyl, 50% dimethyl polysiloxane)
Film Thickness:	0.5 µm
Injection Temperature:	280°C
Injection Mode:	Splitless with solenoid valve open after 1 minute
Transfer Line Temperature:	280°C
Carrier Gas:	He (99.999%)
Gas Head Pressure:	10 psi, flow rate 6 mL/min
Oven Program:	150°C, ramp at 45°/minute to 280°C and hold for 10 minutes
Injection Volume:	2 µL
Autosampler:	Hewlett packard 7673
Retention Time:	11 minutes

Notes: The retention time may vary from one column to the other and also with the length of the column, which will change when the ends of the column are cut for routine maintenance.

3.6 Time Required for Analysis

The time required for a set of 5 samples, 2 recoveries and 1 control is 5-6 hours, plus GC analysis time which can be automated and unattended, provided that no special problems arise, such as matrix interferences.

3.7 Potential Problems

During large analytical sets, the detector sensitivity can vary due to matrix effects. Solvent rinse vials should be placed after each sample injected if this problem arises. It is recommended to condition the column by injecting control extract before starting to inject standards.

4 METHODS OF CALCULATION

4.1 Calibration Procedures

Calculation of results is based on peak height measurements using a calibration curve. To obtain a standard curve, 2 µL of at least three different standard concentrations, e.g. 50, 12.5 and 10 ng/mL of pyridaben are injected. These correspond to 100, 25 and 5 pg 2 µL of pyridaben injected, respectively. The logarithm of the peak height (signal counts) is plotted versus amount of injected standard

4.2 Analyte in Sample

4.2.1 Principle

Calculation of results is based on peak height measurements The amount of pyridaben in injected samples (B) is determined from the calibration curve and the equation described in 4.2.2 is utilized for the determination of the residue (R). Calculation can also be made by a suitable computer program.

At least one fortification and one untreated sample (control) are run with each set of samples. The amount of pyridaben for fortification trials should be on the order of magnitude of the expected residue. The recovery is determined from the fortification experiments (see 4.2.3).

4.2.2 Calculation of Residues

The residue of pyridaben (R) in ppm is calculated by the equation below (example calculation given in Figure 2).

$$R \text{ (ppm)} = \frac{A}{B}$$

where: A = pg value interpolated from calibration curve

B = μg Sample Injected

$$= \frac{\text{Sample Wt.(g) x } \mu\text{L Injected}}{\text{Final dilution volume (mL)}} \times \frac{\text{Aliquot\%}}{100} \times 1000$$

4.2.3 Calculation of Recoveries

Correct fortification results for residues found in the control sample as follows (example calculation given in Figure 3):

ppm (corrected) = ppm in fortified control - ppm in control

Determine percent recovery of pyridaben (BAS 300 I) from the fortification experiments as follows:

$$\% \text{ Recovery} = \frac{\text{ppm (corrected) X 100}}{\text{ppm BAS 300 I}}$$

Only results for procedural recovery samples should be corrected for residues in the controls. Do not correct treated sample results for either control residues or recoveries.

5.1 Accuracy and Precision of Validation Results

Subsamples of control whole apple, dry pomace, wet pomace and apple juice were fortified at levels of 0.05, 0.5 and 5.0 ppm with Pyridaben and were analyzed by Method D9312. The mean recoveries for whole apple, wet pomace, dry pomace and apple juice were: 90±6% (n=17), 96±14% (n=18), 90±8% (n=18) and 95±12% (n=18), respectively. The average recovery for all matrices at all levels was 93±11% (n=71). A summary of the results is given in Table II. Example chromatograms are shown in the Appendix B.

5 2 Quantitation Limit

The quantitation limit for Pyridaben residues in apple and apple process fractions using Method D9312 is 0.05 ppm. At this level, control samples are relatively clean and good recoveries are obtainable. This is the lowest level which is proven by recovery data.

5.3 Ruggedness Testing

Three analysts executed eight analysis sets of apple process fractions. Two sample sets were run for each matrix. Each contained duplicate analyses of the control and triplicate analyses of control fortified with test substance at 0.05, 0.5 and 5.0 ppm levels. The recoveries obtained by each analyst were: 95 ± 10% (n=27), 89 ± 10% (n = 26) and 95 ± 12% (n = 18). This method also has been used for determination of residues in apple process fractions and gave good recoveries and high precision for the fortified samples (Reference 3).

5.4 Limitations

None known to date.

6 CONCLUSIONS

This study has shown that Analytical Method Number D9312 is suitable for measuring residues of pyridaben in apple and apple process fractions down to a quantitation limit of 0.05 ppm. The average recoveries in all matrices were 93±11% (n=71). GC-MSD was used as a confirmatory technique for this method.

Statistical treatment of the validation data included determination of an average and standard deviation. Generally, good recoveries were obtained for the fortified crop matrices at the 0.05, 0.5 and 5.0 ppm levels.

The raw data and final method pertaining to this study are maintained in the BASF Corporation Agricultural Research Center Archives.

7 REFERENCES

1. Abdel-Baky, S., Burkey, J.D., Malinsky, S.D. "Method for Determination of Residues of Pyridaben in Oranges and Oranges Processed Commodities by Gas Chromatography". Method Number D9309. March 1994.

2. Tilting, N. "Stability of Pyridaben Standard Solutions in Different Solvents". BASF Report Number 3817. BASF Registration Number 93/11420.

3. Stewart, J., Abdel-Baky, S., Jackson, S. "Magnitude of Pyridaben Residue in Apple Process Fractions: Ground Application". Report Number A9411. April 1994.

8 SAFETY AND HEALTH CONSIDERATIONS

8.1 General

Use personal protective equipment such as lab coats, safety glasses and gloves (nitrile/latex gloves are recommended) when performing the operations described in this method. Conduct all filtrations, nitrogen-stream evaporations and SPE procedures in a well-ventilated hood. Guard vacuum equipment, such as rotary evaporators, to minimize the possibility of injury caused by flying broken glass. Dispose of hazardous wastes in an environmentally acceptable manner, in compliance with applicable laws and regulations.

8.2 Solvents and Reagents

Review the Material Safety Data Sheets (MSDSs) for all solvents and reagents used in this method.

9. SIGNATURES

We, the undersigned, hereby declare that this study was performed under our supervision according to the procedures described herein, and that this report provides a true and accurate record of the results obtained.

Author/Study Director: Samy Abdel-Baky Date: April 20, 1994

Samy Abdel-Baky, Ph.D.
Agricultural Research Chemist

Approved By: Robert C Paulick Date: April 13, 1994

Robert C. Paulick, Ph.D.
Group Leader, Analytical

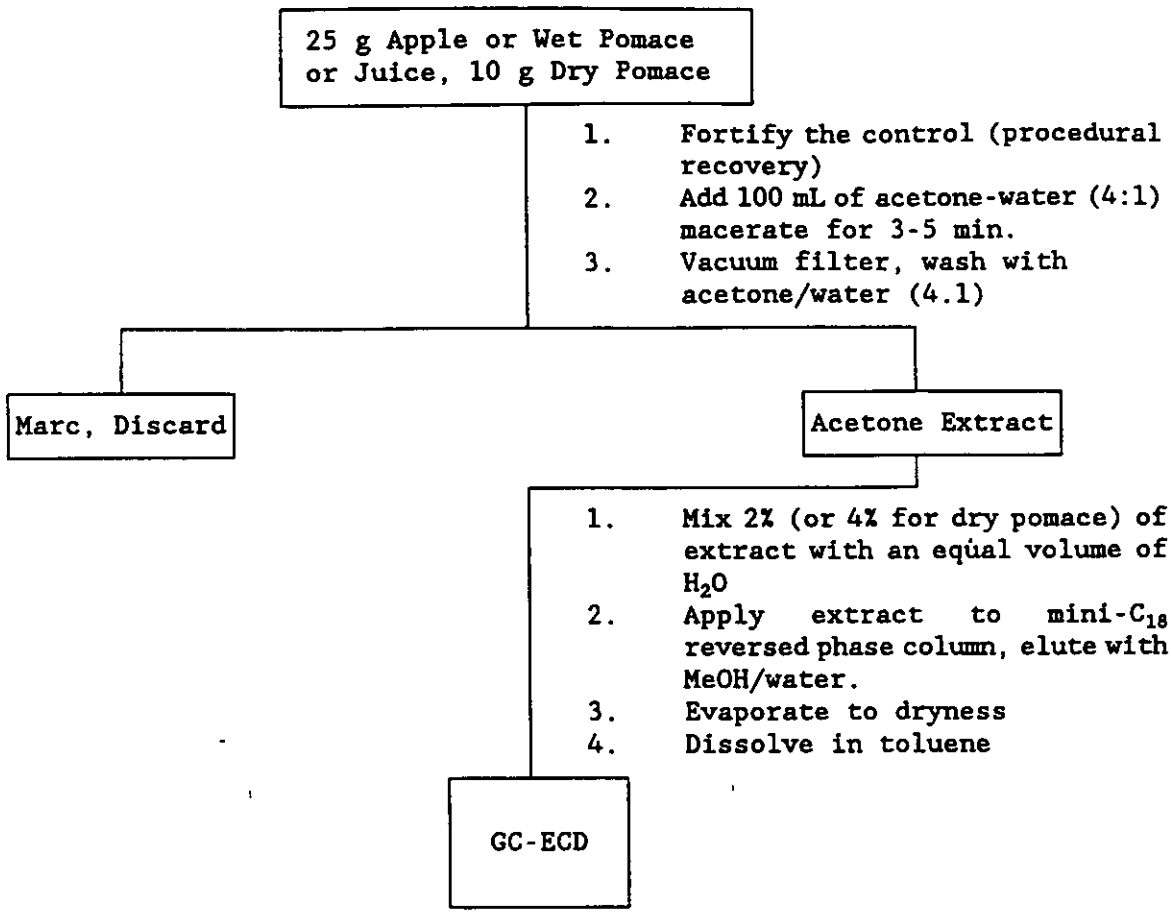


Figure 1 Analytical Procedure for Whole Apple and Apple Process Fractions

BASF Sample Number 9304209, Master Sheet Number 9318604,
Fortified whole apple at 0.05 ppm for pyridaben residue

A = pg value interpolated from standard curve

Standard curve: $\text{Log pg (Pyridaben)} = \frac{\text{Log Peak Height - Intercept}}{\text{Slope}}$

Peak height: 11033

Use full computer precision in any intermediate calculations. Round only the final value.

$$\text{Log pg (Pyridaben)} = \frac{4.0427 - 2.41387}{0.8966} = 1.817$$

A = pg (pyridaben) = $10^{1.817}$ = 65.615 pg

B = µg sample injected

$$= \frac{\text{Sample weight (g)} \times \mu\text{L injected}}{\text{Final dilution volume (mL)}} \times \frac{\text{Aliquot}}{100} \times 1000$$

$$= \frac{25\text{g} \times 2\mu\text{L}}{2\text{mL}} \times \frac{5}{100} \times 1000 = 1250\ \mu\text{g}$$

F = molecular weight conversion factor = 1.0

$$\text{ppm} = \frac{A \times F}{B} = \frac{65.615 \times 1.0}{1250}$$

ppm = 0.052 ppm

If this sample were a typical residue sample, the residue would be reported as 0 052 ppm and there would be no correction for residues in the control sample. See Figure 3 for an example of a recovery calculation in which the final value is corrected for residues in the control.

Figure 2. Typical Residue Calculation

BASF Sample Number 9304209, Master Sheet Number 9318604.

Fortified whole apple at 0.05 ppm for pyridaben recovery.

A - pg value interpolated from standard curve

Standard curve: $\text{Log pg (Pyridaben)} = \frac{\text{Log Peak Height - Intercept}}{\text{Slope}}$

Peak height: 11033

Use full computer precision in any intermediate calculations Round only the final value.

$$\text{Log pg (Pyridaben)} = \frac{4.0427 - 2.41387}{0.8966} = 1.817$$

$$A = \text{pg (pyridaben)} = 10^{1.817} = 65.615 \text{ pg}$$

B - µg sample injected

$$= \frac{\text{Sample weight (g)} \times \mu\text{L injected}}{\text{Final dilution volume (mL)}} \times \frac{\text{Aliquot\%}}{100} \times 1000$$

$$= \frac{25\text{g} \times 2\mu\text{L}}{2\text{mL}} \times \frac{5}{100} \times 1000 = 1250 \ \mu\text{g}$$

F - molecular weight conversion factor = 1.0

$$\text{ppm} = \frac{A \times F}{B} = \frac{65.615 \times 1.0}{1250}$$

ppm = 0.052 ppm

The average control samples is 0.005 ppm of pyridaben residue. (extrapolated below the standard curve).

$$\text{\% Recovery} = \frac{\text{ppm in Fortified Sample - ppm in Control}}{\text{ppm Added to Fortified Sample}} \times 100$$

$$= \frac{0.052 - 0.005}{0.05} \times 100 = 94\%$$

Figure 3. Typical Recovery Calculation

TABLE I. Summary of Recovery Data of Fortified Pyridaben in Apple Samples Using GC-ECD

Matrix	% Recovery (Average ± SD)			Average ± S.D.
	0.05 ppm	0.50 ppm	5.0 ppm	
Whole Apple	94, 92, 96 75, 81	94, 93, 88 98, 91, 89	91, 92, 92 87, 85, 90	90±6 (n=17)
Wet Pomace	90, 100, 132 68, 73, 77	101, 101, 100 93, 98, 97	96, 98, 94 102, 106, 103	96±14 (n=18)
Dry Pomace	105, 91, 92 80, 77, 90	88, 96, 98 76, 86, 87	91, 102, 70 100, 98, 100	90±8 (n=18)
Apple Juice	96, 105, 105 110, 108, 106	90, 80, 63 98, 101, 96	92, 94, 93 99, 99, 82	95 ± 12 (n=18)
Average ± S.D.	93±15 (n=23)	92±9 (n=24)	94±8 (n=24)	
Total Average ± S.D.			93±11 (n=71)	

Table II. Individual Recovery Data of Fortified Pyridaben in Apples and Apple Processed Fractions

Fortified level (ppm)[1]	Master Sheet Number	Final Volume (mL)	Sample Weight Injected (mg)[2]	Peak Height (µV)	Residue (ppm)[3]	Recovery (%)[4]
0 05	9318604 Whole Apple	2 0	1 25	11033, 10814, 11194	0 052, 0 051, 0.053	94, 92, 96
0 50		10 0	0 25	18775, 18656, 17798	0 474, 0.471, 0 447	94, 93, 88
5 00		50 0	0.05	33763, 33944, 33924	4.57, 4.59, 4.59	91, 92, 92
0 05	9318607 Whole Apple	2 0	0 50	9152, 9647	0 050, 0 053	75, 81
0 50		10	0 10	17330, 16124, 15811	0 504, 0 465, 0 455	98, 91, 89
5 00		100	0 01	15152, 14901, 15746	4 34, 4.26, 4.53	87, 85, 90
0 05	9318605 Dry Pomace	1 0	2 00	39583, 37725, 37921	0 135, 0 128, 0 129	105, 91, 92
0 50		10	0.20	16320, 17733, 17856	0 521, 0 570, 0 574	88, 96, 98
5 00		50	0 04	27851, 30867, 21977	4.63, 5 17, 3 59	91, 102, 70
0 05	9318612 Dry Pomace	3 0	0 267	5221, 5091, 5763	0 040, 0 039, 0 045	80, 77, 90
0 50		10	0 08	12784, 14185, 14372	0.380, 0 429, 0 436	76, 86, 87
5 00		100	0 008	16190, 15833, 16208	5 01, 4.88, 5 02	100, 98, 100
0.05	9318602 Wet Pomace	2 0	1.25	10225, 11213, 14072	0 051, 0.056, 0.072	90, 101, 132
0 50		10 0	0 25	19401, 19552, 19379	0.508, 0 512, 0 507	101, 101, 100
5 00		50.0	0 05	34817, 35368, 34154	4 81, 4.89, 4 71	96, 98, 94
0 05	9318613 Wet Pomace	2 0	0 50	2145, 2251, 2338	0.047, 0 050, 0.052	68, 73, 77
0 50		10	0 10	4009, 4226, 4170	0.476, 0 505, 0 497	93, 98, 97
5 00		100	0 01	4284, 4404, 4322	5.13, 5 29, 5.18	102, 106, 103
0 05	9318611 Apple Juice	2 0	0 50	7851, 8481, 8470	0 051, 0 055, 0 055	96, 105, 105
0 50		10	0 10	12959, 11676, 9599	0 454, 0 402, 0 320	90, 80, 63
5 00		100	0 01	13100, 13347, 13251	4 59, 4.69, 4 65	92, 94, 93
0 05	9318614 Apple Juice	2 0	0 50	11642, 11508, 11267	0 055, 0 054, 0 053	110, 108, 106
0 50		10	0 10	19019, 19460, 18659	0 492, 0 506, 0 481	98, 101, 96
5 00		100	0 01	19152, 19075, 16227	4 96, 4 94, 4 08	99, 99, 82

Table II. Individual Recovery Data of Fortified Pyridaben in Apples and Apple Processed Fractions (continued).

FOOTNOTES

[1]Fortification of Pyridaben was added prior to extraction. The fortifications were run concurrently with control samples.

[2]Sample Weight Injected (mg) = $\frac{\text{g Sample x } \mu\text{L Injected}}{\text{Dilution Volume (mL)}} \times \frac{\text{Aliquot \%}}{100}$

[3]Residue (ppm) = $\frac{\text{ng Analyte Found}}{\text{mg Sample Injected}}$ x Molecular Weight Conversion Factor (F)

Molecular Weight conversion factor = $\frac{\text{Molecular Weight of the Fortified Standard}}{\text{Molecular Weight of the Final Analyte}}$

e.g. for pyridaben

Molecular Weight Conversion Factor (F) = $\frac{364.9}{364.9} = 1.0$

[4]Recovery % = $\frac{\text{ppm Found in Fortified Sample - ppm Found in Control}}{\text{ppm Added to Fortified Sample}} \times 100$

The following values were constant for all analyses:
a) Sample size was 25.0 g (except for dry pomace = 10 g).
b) Injection volume was 2 μL.

Values in this table have been rounded off for reporting purposes, but not for any further calculations.

Table III. Summary of the Standard Data for Pyridaben in Apple PFs Using GC-ECD

Master Sheet Number	Peak Height (μV)				Calibration Curve Data[1]	
	Level 1 (50 pg)	Level 2 (100 pg)	Level 3 (200 pg)	Level 4 (300 pg)	Slope	Intercept
9318604	8551 8699 8571	16091 16563 16043	30318 30099 29850	43064 43058 42590	0.89660	2.41387
9318605	7679 8365 8587	14879 16051 16460	29425 29931 31000	42103 43773 44347	0.93098	2 33405
9318602	7720 8402 8571	14893 15928 16155	29313 29797 29662	42162 42334 42760	0.91687	2.35894

Master Sheet Number	Peak Height (μV)				Calibration Curve Data[1]	
	Level 1 (10 pg)	Level 2 (25 pg)	Level 3 (50 pg)	Level 4 (100 pg)	Slope	Intercept
9318607	4048 3955 3980	9253 9413 9212	17463 17197 17122	32810 32238 30949	0.90319	2.70124
9318611	3339 3649 3551	7288 8062 8075	13848 14634 14411	25388 25399 25018	0.85930	2.68903
9318612	5257 4684 4863	11094 10691 10968	19548 19407 19697	34667 35151 35822	0.85313	2.84180
9318613	955 990 1116*	2121 2248 2365	3932 4283 4373	7770 7501 8046	0.88376	2.12076
9318614	4834 5312 4667	11206 10708 10837	19308 18792 19484	34641 33991 34754	0.84236	2.85390

[1]The formula for the calibration curve is:

$$\text{pg Analyte} = \frac{(\text{Peak Height} - \text{Intercept})}{\text{Slope}}$$

TABLE IV. Pesticides Used for the Citrus and Pome Fruit Specificity Study

40CFR180	CHEMICAL	TOLERANCE[1]		ANALYSIS RESULTS[2]
		CITRUS FRUIT	POME FRUIT	
103	CAPTAN	---	25	I
.105	DEMETON	0.75	0.75	I
.106	DIURON	1(4)	1	I
.108	ACEPHATE	4	---	I
.109	CHLORBENZILATE	5	---	I
.110	MANEB	---	2	NR
.111	MALATHION	8(50)	8	I
.113	ALLETHRIN	4	4	I
114	FERBAM	7	7	NR
.115	ZINEB	7	7	NR
116	ZIRAM	---	7	I
.117	EPTC	0 1	---	I
118	DICHLONE	---	3	I
120	METHOXYCHLOR	---	14	I
.121	PARATHION (ETHYL)	1	1	I
.123	INORGANIC BROMIDES (METHYL BROMIDE)	30	5	NR
124	GLYODIN	---	5	I
127	PIPERONYL BUTOXIDE	8	8	I
128	PYRETHRINS	1	1	I
129	o-PHENYLPHENOL	10	25	I
.130	HYDROGEN CYANIDE	50	---	NR
.132	THIRAM	---	7	I
.133	LINDANE	0.5	1	I
.139	PERTHANE	---	15	NA
.141	BIPHENYL	110	---	I
.142	2,4-D	5	5	x
.144	CYHEXATIN	2(8)	2(8)	NR
.145	FLUORINE COMPOUNDS	7	7	NA
150	DALAPON	5(20)	3	I
.153	DIAZINON	---	0 5	I
154	AZINPHOSMETHYL[3]	2	2	I
155	NAPHTHALENE ACETIC ACID	0.1	1	NR
156	CARBOPHENOTHION (TRITHION)	2	0 8	I
157	MEVINPHOS	0.2	0.5	I
161	MANGANOUS DIMETHYLDITHIOCARBAMATE	---	7	NR
.163	DICOFOL	10	5	I
167	NICOTINE COMPOUNDS	2	2	I
.169	CARBARYL	10	10	I
.170	TEMEPHOS (ABATE)	0.1	---	I
.171	cis-DIOXATHION	3(18)	5	NA
.172	DODINE	---	5	NR
.173	ETHION	2(10)	2	I
.174	TETRADIFON	2	5	I
176	ZINC-MANEB COMPLEX	---	10	NR
178	ETHOXYQUIN	---	3	NA
179	TARTER EMETIC	3.5	---	NR
.182	ENDOSULFAN	---	2	I
188	AMMATE	---	5	NR
190	DIPHENYLAMINE	---	10	I
191	FOLPET	15	25	I
198	TRICHLORFON	0 1	---	NA
204	DIMETHOATE	2	2	I
.205	PARAQUAT	0 05	0.05	NR
207	TRIFULURALIN	0 05	---	I
.209	TERBACIL	0 1	0.1	I
210	BROMACIL	0.1	---	I
213	SIMAZINE	0 25	0.25	I

TABLE IV. Pesticides Used for the Citrus and Pome Fruit Specificity Study (continued)

40CFR180	CHEMICAL	TOLERANCE[1]		ANALYSIS RESULTS[2]
		CITRUS FRUIT	POME FRUIT	
215	NALED	3	0.05	I
217	POLYRAM	---	2	NR
219	TIBA	---	0 05	NR
224	GIBBERELLIC ACID	0 15	0 5	NR
225	ALUMINUM PHOSPHIDE	0 01	0.01	NR
226	DIQUAT DIBROMIDE	---	0 02	NR
.230	DIPHENAMID	---	0.1	I
231	DICHLOBENIL	0 15	0.15	I
239	PHOSPHAMIDON	0 75	1	I
242	THIABENDAZOLE	10(35)	10(33)	I
.245	STREPTOMYCIN	---	0 25	NR
246	DAMINOZIDE	---	5	NR
252	GARDONA	---	10	NA
253	METHOMYL	2	4	I
258	AMETRYN	0 1	---	I
259	PROPARGITE	5	3(80)	I
261	IMIDAN	5	10	I
263	PHOSALONE	3(12)	10(85)	I
267	CAPTOFOL	0.5	0.25	I
269	ALDICARB	0 3(0 6)	---	I
271	BORON	8	---	NR
276	FORMETANATE HYDROCHLORIDE	4(10)	3	NR
281	DINOSEB	0.1	0.1	I
287	AMITRAZ	---	3	I
289	METHANEARSONIC ACID (MAA)	0 35	---	NR
.294	BENOMYL	10(50)	7(70)	I
298	METHIDATHION	6	0 05	I
300	ETHEPHON	2	5	NR
303	OXAMYL	3	2	I
304	ORYZALIN	0 05	0.05	I
309	ALPHA-NAPHTHALENEACETAMIDE	---	0 1	I
317	PRONAMIDE	---	0 1	I
.320	METHIOCARB	0 02	---	I
321	sec-BUTYLAMINE HCl SALT	30(90)	---	NR
326	DIALIFOR	3	1.5	NA
328	NAPROPAMIDE	0 1	0 1	I
.330	OXYDEMETON METHYL	1	1	I
.336	CYCLOHEXIMIDE	0 1	---	I
.337	OXYTETRACYCLINE	---	0.35	NA
338	OXYTHIOQUINOX	0 5	0.05	I
341	DINOCAP	---	0 1(0 3)	I
342	CHLORPYRIFOS	1(25)	1.5	I
344	4,6-DINITRO-o-CRESOL	---	0 02	I
346	OXYDIAZON	---	0.05	I
347	TEPP	0 01	0 01	NA
349	FENAMIPHOS	0 6(25)	0 25(5)	I
356	NORFLURAZON	0 2(1)	0.1	I
362	HEXAKIS	20(35)	15(75)	NA
364	GLYPHOSATE	0 2(1)	0 2	NR
371	THIOPHANATE METHYL[3]	---	7(40)	I
375	MAGNESIUM PHOSPHIDE	0 01	0.01	NR
376	6-BENZYLADENINE	---	0 15	I
378	PERMETHRIN[3]	---	3	I
379	FENVALERATE	---	2(20)	I
381	OXYFLUORFEN	---	0 05	I
382	TRIFORINE	---	0 01	I
400	FLUCYTHRINATE	---	1(10)	I
408	METALAXYL	1(7)	0 2(2)	I
410	TRIADIMEFON	---	1(4)	I
412	SETHOXYDIM	0 5(1 5)	0 2(0 8)	NR

TABLE IV. Pesticides Used for the Citrus and Pome Fruit Specificity Study (continued)

40CFR180	CHEMICAL	TOLERANCE[1]		ANALYSIS RESULTS[2]
		CITRUS FRUIT	POME FRUIT	
.413	IMIZALIL FREE BASE	10(25)	---	I
.415	FOSETYL-AL	0 5	---	NR
420	FLURIDONE	0.1	0 1	I
421	FENARIMOL	---	0.1(2)	I
443	MYCLOBUTANIL	---	0.5(5)	I
446	CLOFENTEZINE	---	0 5(20)	I
.448	HEXYTHIAZOX	---	0.3	NA
467	CARBON DISULFIDE	0.1	---	NR
Total	125 Compounds			

[1]The values in parentheses are the maximum food additive tolerances for that compound.

[2]I - Injected into GC-ECD
NR - Not run by GC (salts and inorganic compounds)
NA - Not available from standard sources

[3]Compounds were detected within the retention time window of pyridaben (9 47±0.15 minute). These compounds showed no interferences with pyridaben after the cleanup step (mini-silica and mini-C_{18} columns).

APPENDIX A

Deviations and Amendments to Protocol

APPENDIX A
Changes to Protocol Number 93186

During the course of the study, several changes to the protocol were documented.

Amendments

1. Amendment Number 1

   An additional sample number (9) was added for untreated whole apple (control).

   Reason: The original sample number (1) for untreated whole apple was sent to the processor.

2. Amendment Number 2

   The evaporation step was eliminated and consequently, C_{18} column conditioning, loading and washing steps were adjusted.

   Reason: To eliminate the fluctuation in the recoveries of the fortified samples and make the method more rugged.

3. Amendment Number 3

   A method specificity phase was added to determine if any pesticides registered for use on pome fruits or citrus fruits interfere with pyridaben (BAS 300 I) analysis by GC-ECD.

   Reason: To fulfill the requirement for registration under EPA guidelines (Pesticide Assessment Guidelines, Subdivision O, Residue Chemistry, Series 171-4(I), Analytical Method).

Deviations

There was one deviation to the protocol. The protocol for this study stated that if modifications to the method were necessary, they would be detailed by amendment. The scope of those modifications was meant to include only technical changes to the procedures in the method. Changes in the wording of the method or the addition of sections to the method which were left out of the draft for the sake of brevity were not detailed by amendment and were not intended to be.

Reason: The draft method provided with the protocol was not meant to be a nearly complete document, but instead a document to provide the technical procedures to be validated.

These changes had no adverse impact on the validity of the study

APPENDIX B

Typical Raw Data and Chromatograms

Description

Figure 1 Typical GC parameters.

Figure 2 Typical chromatogram of a 10 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

Figure 3 Typical chromatogram of a 25 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III

Figure 4 Typical chromatogram of a 50 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

Figure 5 Typical chromatogram of a 100 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

Figure 6 Typical standard Curve for 10, 25, 50 and 100 pg amounts of pyridaben. Data from these standards can be found in Table III.

Figure 7 Typical chromatogram of a control whole apple sample. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

Figure 8 Typical chromatogram of a control whole apple sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

Recovery = 94%

Figure 9 Typical chromatogram of a control whole apple sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

Recovery = 93%

Figure 10 Typical chromatogram of a control whole apple sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

Recovery = 91%

Figure 11 Typical chromatogram of a control wet pomace sample. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

Description (continued)

Figure 12 Typical chromatogram of a control wet pomace sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

Recovery = 101%

Figure 13 Typical chromatogram of a control wet pomace sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

Recovery = 101%

Figure 14 Typical chromatogram of a control wet pomace sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

Recovery = 98%

Figure 15 Typical chromatogram of a control dry pomace sample. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

Figure 16 Typical chromatogram of a control dry pomace sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

Recovery = 80%

Figure 17 Typical chromatogram of a control dry pomace sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

Recovery = 86%

Figure 18 Typical chromatogram of a control dry pomace sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

Recovery = 100%

Figure 19 Typical chromatogram of a control apple juice sample. Sample number 9304206 from master sheet number 9318611 Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

Description (continued)

Figure 20 Typical chromatogram of a control apple juice sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

Recovery = 96%

Figure 21 Typical chromatogram of a control apple juice sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

Recovery = 90%

Figure 22 Typical chromatogram of a control apple juice sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

Recovery = 94%

Figure 1 Typical GC parameters.

INSTRUMENT PARAMETERS

(BAS 300 I)

Date: 12-20-93 Initial: DSM

Study No.: 93186 Master Sheet No.: 93186011

GC INFORMATION:

GC Model:	HP 5890 (older)			
BASF No.:	54	VG Channel:	2	
Sequence Name:	BAS300I	Method Name:	BAS300I	
Detector Type:	ECD	Range/Atten:	0/0	Zero: 5.0
Injector:	A			

GAS FLOWS:

Detector Hydrogen:	NOT APPLICABLE
Detector Air:	NOT APPLICABLE
Nitrogen Make-up:	104 mL/min N_2 (including column flow)
Carrier Gas:	Hydrogen
Column Head Pressure:	10.0 psi H_2
Column Flow Rate:	4.0 mL/min. (at 70°C)
Split Vent Flow:	30 mL/min. Septum Purge: 0.6 mL/min.

COLUMN:

Column Phase:	DB-17	Serial No.:	2322925		
Column Length:	30 m	Column ID:	0.32 mm	Film Thickness:	0.25 µm

HEATED ZONES:

Oven Initial Temp. : 70°C Initial Hold Time: 0.5 min.

Rate #1:	50°C/min.	Final Temp. 1:	235°C	Hold 1:	4.0 min.
Rate #2:	25°C/min.	Final Temp. 2:	275°C	Hold 2:	3.0 min.
Rate #3:	60°C/min.	Final Temp. 3:	295°C	Hold 3:	5.0 min.

Injector Temperature:	185°C
Detector Temperature:	325°C
Equilibration Time:	2.0 min.

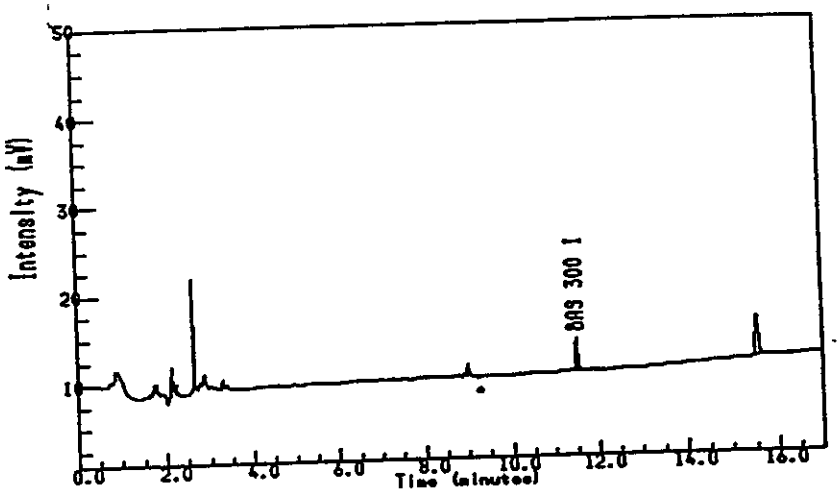
COMMENTS:

1. 0.5 min. splitless (Purge ON at 0.5 min., OFF at 17.5 min.)
2. Expected Retention Time. 11.60 +/-0 05 min.
3. Injection Volume. 2.0 µL

Figure 2 Typical chromatogram of a 10 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

[93186] 2 B9318611,11,1
Reported on 20-DEC-1993 at 15:02
DSM

Acquired on 18-DEC-1993 at 16:05



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 10 PG STD
Sample Id :
Sample Type : Standard Amount=1.00000
Bottle No : 15

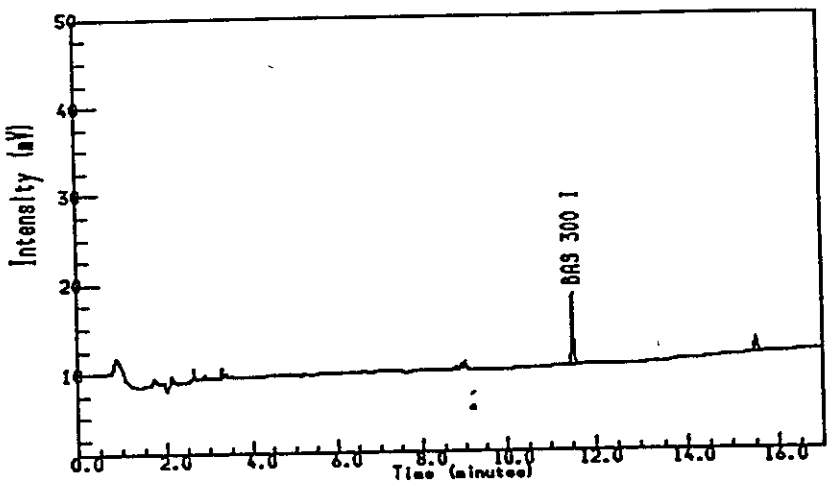
PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
11.509	3649	10.378	BAS 300 I
15.525	4645	0.000	
Totals			
Unknowns	0	N/A	
	8294	10.378	
	8294	10.378	

Figure 3 Typical chromatogram of a 25 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

[93186] 2 B9318611,14,1
Reported on 20-DEC-1993 at 15:03
BSM

Acquired on 18-DEC-1993 at 17:18



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 25 PG STD
Sample Id :
Sample Type : Standard Amount=1.00000
Bottle No : 2

PEAK INFORMATION

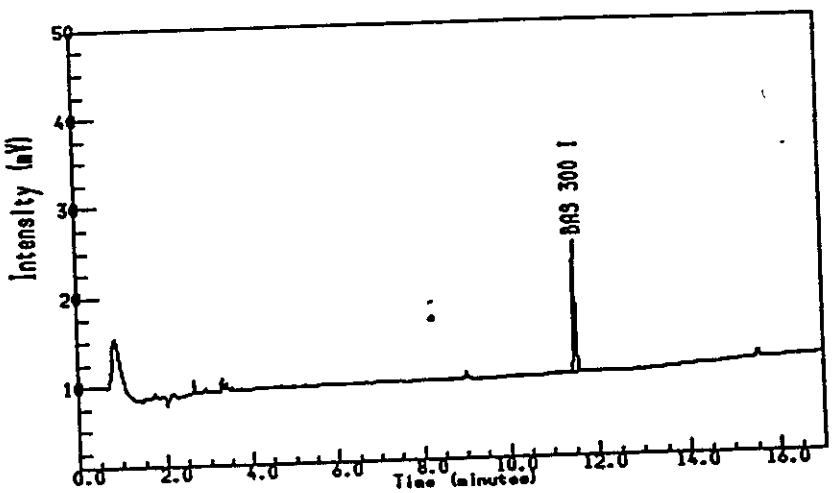
RT mins	Hght uV	ppb	Peak name
11.504	8062	26.109	BAS 300 I
15.520	1626	0.000	

Totals		
Unknowns	0	N/A
	9688	26.109
	9688	26.109

Figure 4 Typical chromatogram of a 50 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

[93186] 2 B9318611,17,1
Reported on 20-DEC-1993 at 15:03
DSM

Acquired on 18-DEC-1993 at 18:31



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 50 PG STD
Sample Id :
Sample Type : Standard Amount=1.00000
Bottle No : 5

PEAK INFORMATION

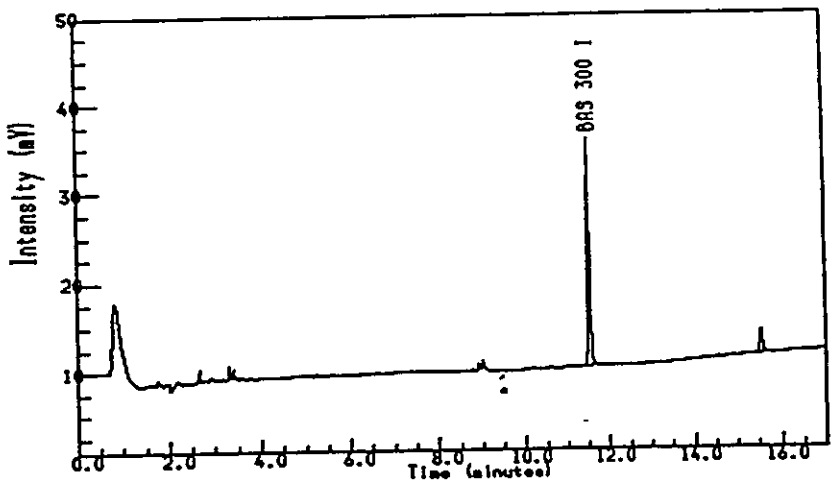
RT mins	Hght uV	ppb	Peak name
11.509	14634	52.248	BAS 300 I

Totals		
Unknowns	0	N/A
	14634	52.248
	14634	52.248

Figure 5 Typical chromatogram of a 100 pg standard pyridaben from master sheet number 9318611. Data from this standard can be found in Table III.

[93186] 2 B9318611,19,1
Reported on 20-DEC-1993 at 15:03
DSM

Acquired on 18-DEC-1993 at 19:19



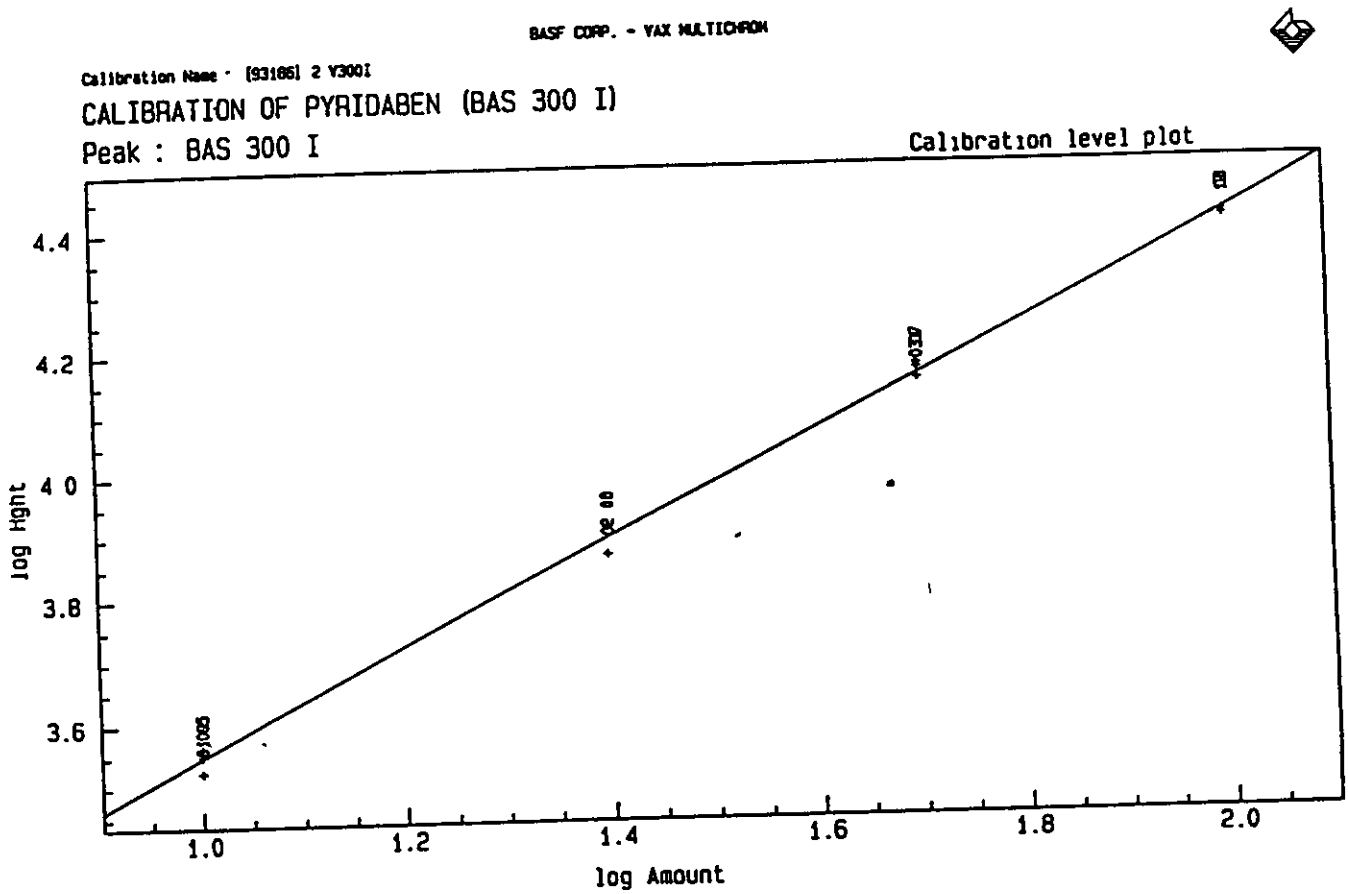
BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 100 PG STD
Sample Id :
Sample Type : Standard Amount=1.00000
Bottle No : 18

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
11.525	25399	99.254	BAS 300 I
15.541	2749	0.000	
Totals			
Unknowns	0	N/A	
	28148	99.254	
	28148	99.254	

Figure 6 Typical standard Curve for 10, 25, 50 and 100 pg amounts of pyridaben. Data from these standards can be found in Table III.



Constant : 2.68903
1st degree : 0.85930

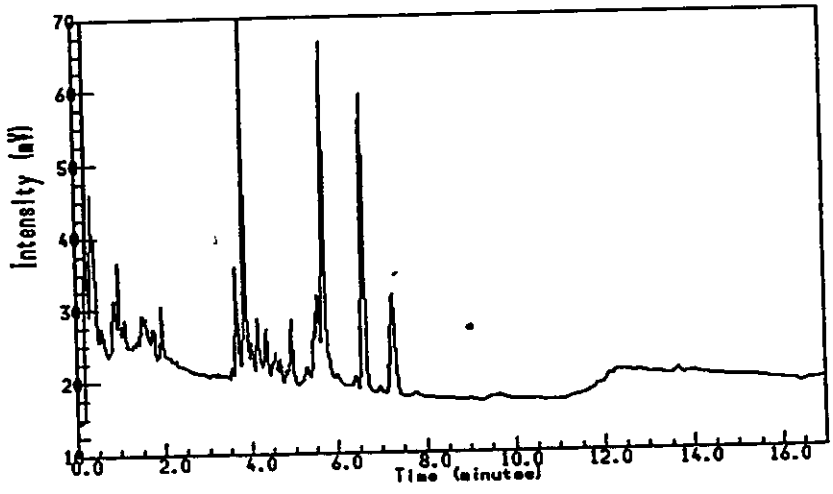
Curve fit : Linear
Correlation coefficient : 0.99891
Standard error : 0 01626
Reported on 20-DEC-1993 at 14.20

DSM
MS = 93186011
RS = B93186011

Figure 7 Typical chromatogram of a control whole apple sample. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

{93186} 1 9318604,6,1
Reported on 3-DEC-1993 at 13:20
Modified on 3-DEC-1993 at 13:01

Acquired on 3-DEC-1993 at 05:01



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : CONTROL APPLE B
Sample Id : 9304209
Sample Type : Control Amount=1.00000
Bottle No : 4

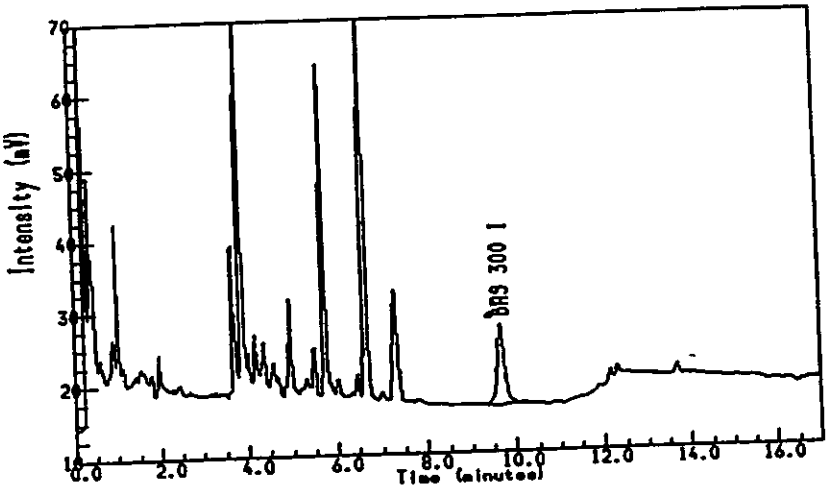
PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
Totals			
Unknowns	0	N/A	
	0	0.000	
	0	0.000	

Figure 8 Typical chromatogram of a control whole apple sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

[93186] 1 9318604,9,1
Reported on 3-DEC-1993 at 13:21 MTW
Modified on 3-DEC-1993 at 13:01

Acquired on 3-DEC-1993 at 06:04



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 0.05 PPM A
Sample Id : 9304209
Sample Type : Recovery Amount=1.00000
Bottle No : 6

PEAK INFORMATION

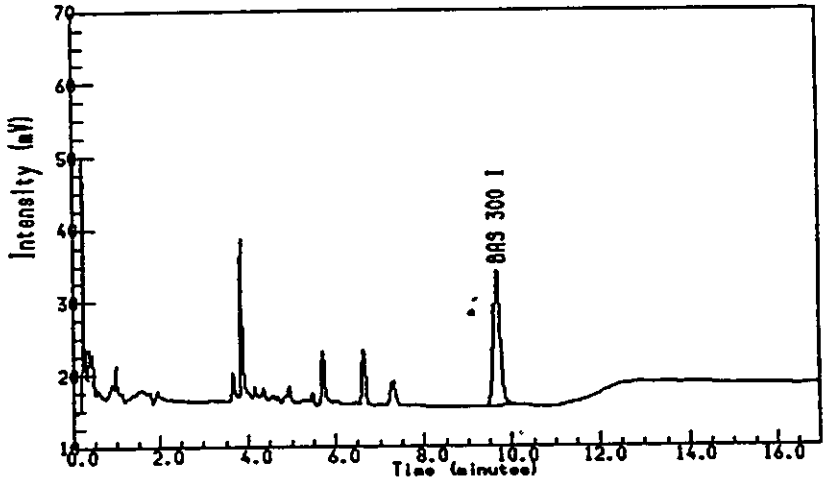
RT mins	Hght uV	ppb	Peak name
9.675	11033	52.449	BAS 300 I

Totals		
Unknowns	0	N/A
	11033	52.449
	11033	52.449

Figure 9 Typical chromatogram of a control whole apple sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

[93186] 1 9318604,20,1
Reported on 3-DEC-1993 at 13:22
Modified on 3-DEC-1993 at 13:01

Acquired on 3-DEC-1993 at 09:55



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 0.50 PPM B
Sample Id : 9304209
Sample Type : Recovery Amount=1.00000
Bottle No : 19

PEAK INFORMATION

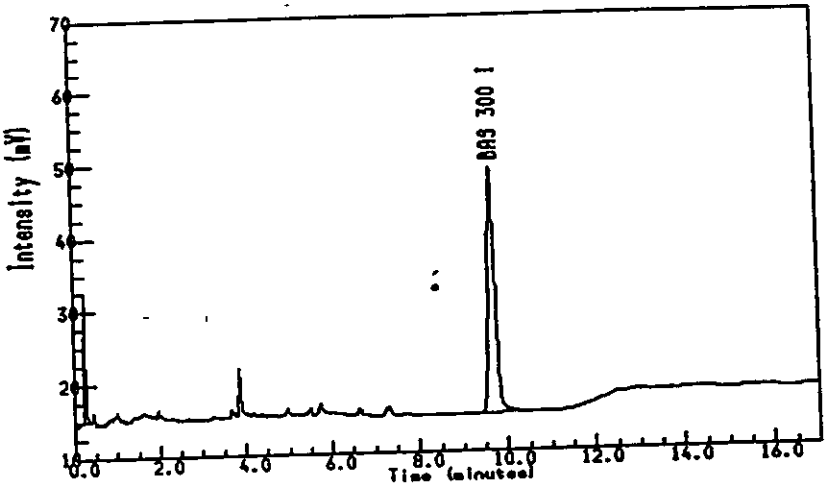
RT mins	Hght uV	ppb	Peak name
9.669	18656	471.152	BAS 300 I

Totals		
Unknowns	0	N/A
	18656	471.152
	18656	471.152

Figure 10 Typical chromatogram of a control whole apple sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304209 from master sheet number 9318604. Data for this sample can be found in Table II.

[93186] 1 9318604,24,1
Reported on 3-DEC-1993 at 13:22
Modified on 3-DEC-1993 at 13:01 MTW

Acquired on 3-DEC-1993 at 11:20



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 5.0 PPM A
Sample Id : 9304209
Sample Type : Recovery Amount=1.00000
Bottle No : 17

PEAK INFORMATION

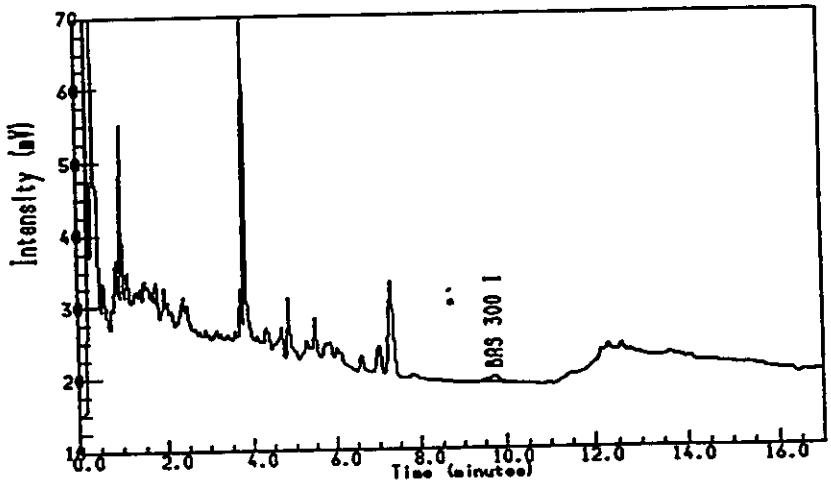
RT mins	Hght uV	ppb	Peak name
9.685	33763	4565.147	BAS 300 I

Totals		
Unknowns	0	N/A
	33763	4565.147
	33763	4565.147

Figure 11 Typical chromatogram of a control wet pomace sample. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

[93186] 1 9318602,6,1
Reported on 1-DEC-1993 at 07:57 MTW
Modified on 1-DEC-1993 at 07:47

Acquired on 30-NOV-1993 at 18:47



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : CONTROL APPLE B
Sample Id : 9304~~206~~ 307 ③ SA 12-8-93
Sample Type : Control Amount=1.00000
Bottle No : 4

PEAK INFORMATION

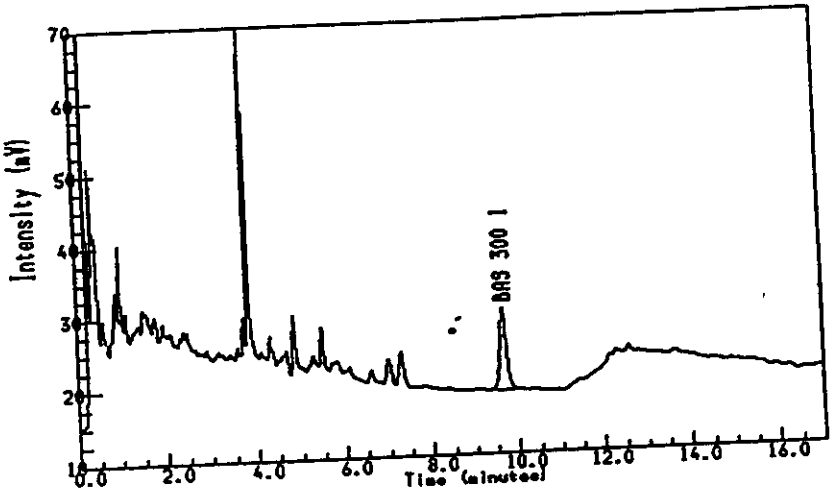
RT mins	Hght uV	ppb	Peak name
9.717	1042	4.184	BAS 300 I

Totals		
Unknowns	0	N/A
	1042	4.184
	1042	4.184

Figure 12 Typical chromatogram of a control wet pomace sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

[93186] 1 9318602,12,1
Reported on 1-DEC-1993 at 07:58
Modified on 1-DEC-1993 at 07:47 MTW

Acquired on 30-NOV-1993 at 20:53



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 0.05 PPM B
Sample Id : 9304206307 ③ SA 12-8-93
Sample Type : Recovery Amount=1.00000
Bottle No. : 7

PEAK INFORMATION

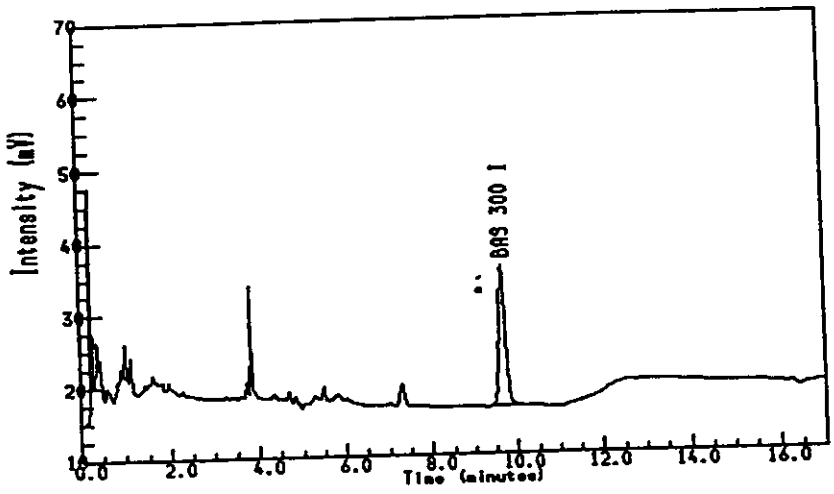
RT mins	Hght uV	ppb	Peak name
9.669	11213	55.871	BAS 300 I

Totals		
Unknowns	0	N/A
	11213	55.871
	11213	55.871

Figure 13 Typical chromatogram of a control wet pomace sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

[93186] 1 9318602,18,1
Reported on 1-DEC-1993 at 07:58
Modified on 1-DEC-1993 at 07:47 MTW

Acquired on 30-NOV-1993 at 22:59



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 0.50 PPM A
Sample Id : 9304~~206~~ 307 ③ SA 12-8-93
Sample Type : Recovery Amount=1.00000
Bottle No : 13

PEAK INFORMATION

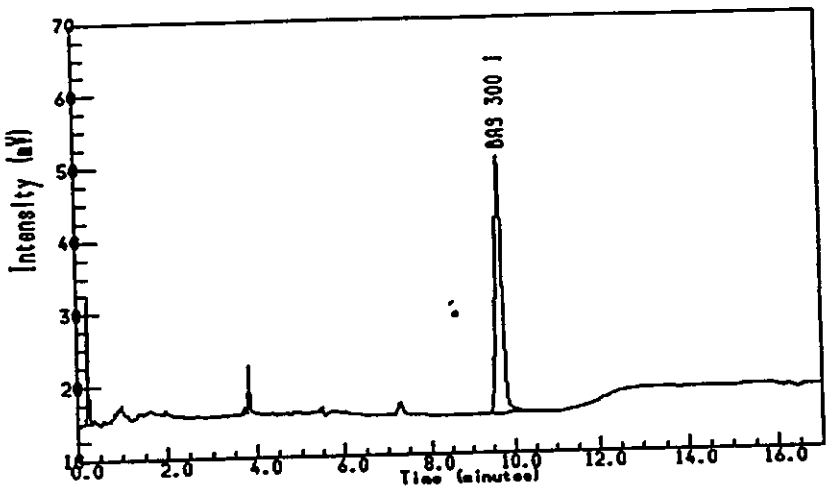
RT mins	Hght uV	ppb	Peak name
9.669	19401	507.964	BAS 300 I

Totals		
Unknowns	0	N/A
	19401	507.964
	19401	507.964

Figure 14 Typical chromatogram of a control wet pomace sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304307 from master sheet number 9318602. Data for this sample can be found in Table II.

[93186] 1 9318602,26,1
Reported on 1-DEC-1993 at 07:59
Modified on 1-DEC-1993 at 07:47 MTW

Acquired on 1-DEC-1993 at 01:47



BASF CORP. - VAX MULTICHROM

Analyst Name : MICHAEL WHITE
Lims Id :
Comment :
Method Title :
Sample Name : 5.0 PPM B
Sample Id : 9304~~206~~307 ③SA 12-8-93
Sample Type : Recovery Amount=1.00000
Bottle No : 18

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
9.664	35368	4889.085	BAS 300 I

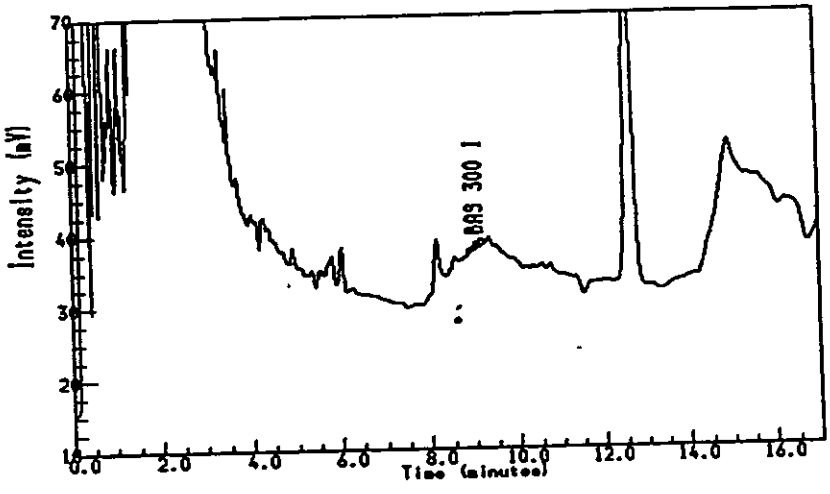
Totals		
Unknowns	0	N/A
	35368	4889.085
	35368	4889.085

Figure 15 Typical chromatogram of a control dry pomace sample. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

[93186] 1 C9318612,6,1
Reported on 29-DEC-1993 at 09:42

DSM

Acquired on 28-DEC-1993 at 12:56



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : CONTROL B D.P.
Sample Id : 9304308
Sample Type : Control Amount=1.00000
Bottle No : 4

PEAK INFORMATION

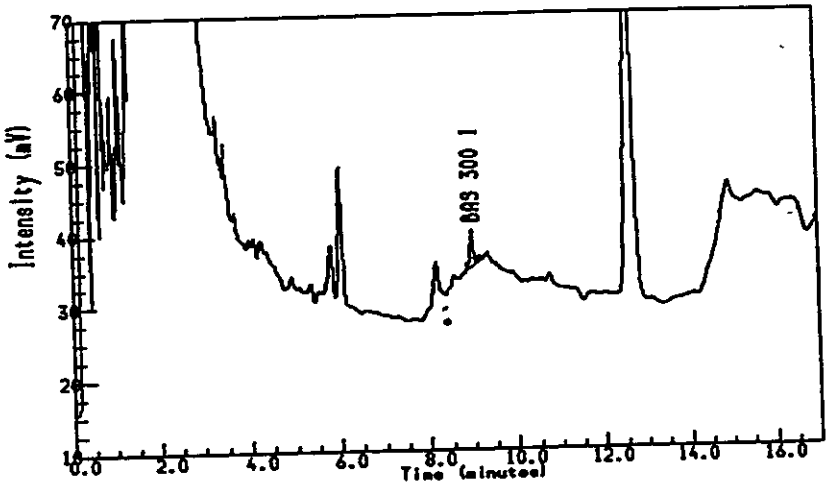
RT mins	Hght uV	ppb	Peak name
8.896	861	0.000	
9.029	1240	4.932	BAS 300 I
9.152	1138	0.000	

Totals		
Unknowns	0	N/A
	3239	4.932
	3239	4.932

Figure 16 Typical chromatogram of a control dry pomace sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

[93186] 1 C9318612,9,1
Reported on 29-DEC-1993 at 09:43

Acquired on 28-DEC-1993 at 14:04



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 0.05 PPM A
Sample Id : 9304308
Sample Type : Recovery Amount=1.00000
Bottle No : 6

PEAK INFORMATION

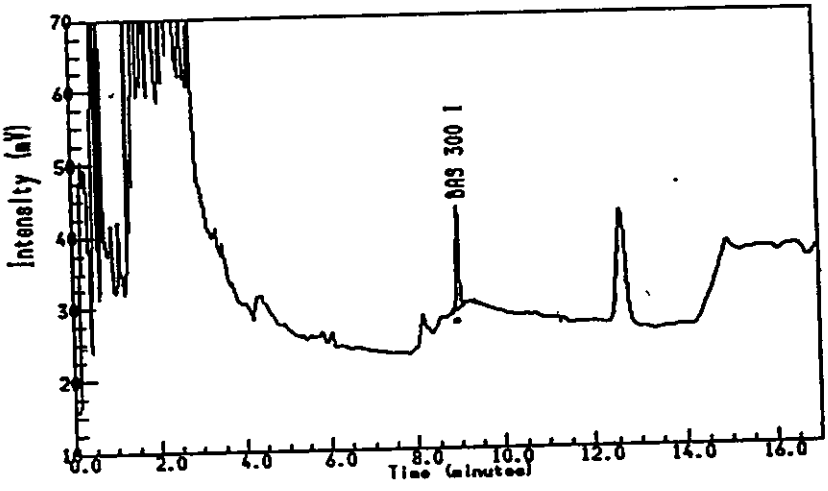
RT mins	Hght uV	ppb	Peak name
8.976	5221	39.881	BAS 300 I
9.147	831	0.000	
Totals			
Unknowns	0	N/A	
	6051	39.881	
	6051	39.881	

Figure 17 Typical chromatogram of a control dry pomace sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

[93186] 1 C9318612,20,1
Reported on 29-DEC-1993 at 09:44

DSM

Acquired on 28-DEC-1993 at 18:12



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 0.50 PPM B
Sample Id : 9304308
Sample Type : Recovery Amount=1.00000
Bottle No : 19

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
8.976	14185	428.998	BAS 300 I
9.344	361	0.000	

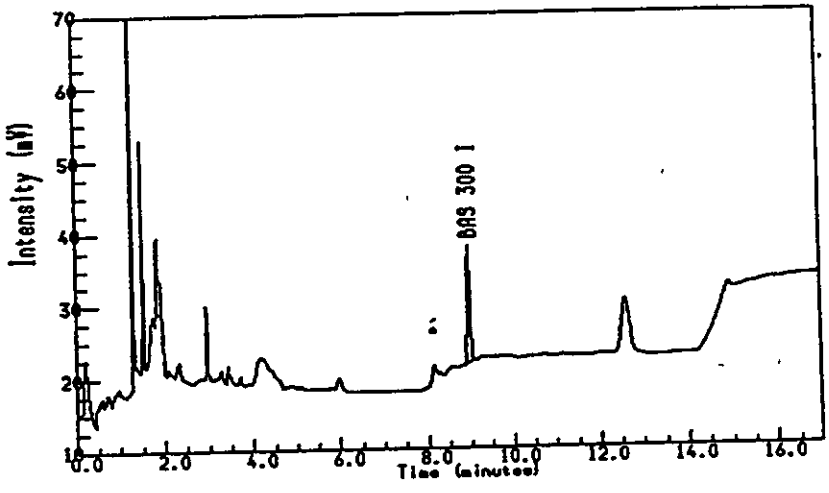
Totals		
Unknowns	0	N/A
	14545	428 998
	14545	428.998

Figure 18 Typical chromatogram of a control dry pomace sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304308 from master sheet number 9318612. Data for this sample can be found in Table II.

[93186] 1 C9318612,27,1
Reported on 29-DEC-1993 at 09:44

DSM

Acquired on 28-DEC-1993 at 20:50



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 5.0 PPM C
Sample Id : 9304308
Sample Type : Recovery Amount=1.00000
Bottle No : 23

PEAK INFORMATION

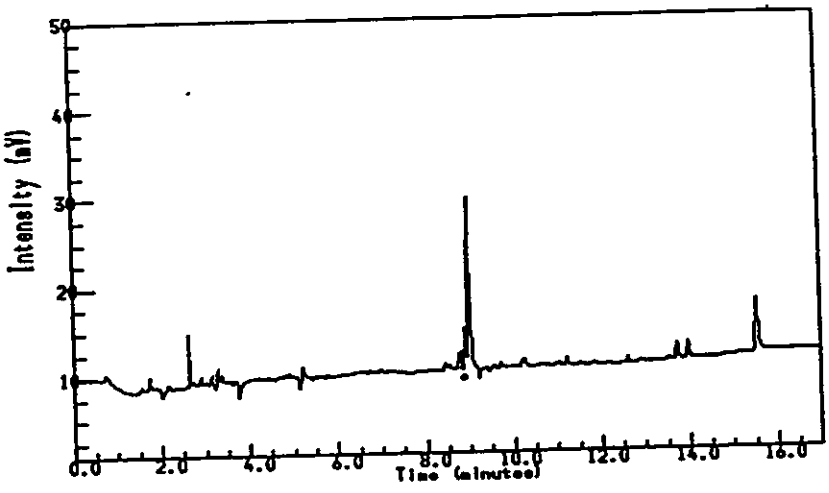
RT mins	Hght uV	ppb	Peak name
8.960	16208	5015.829	BAS 300 I

Totals		
Unknowns	0	N/A
	16208	5015.829
	16208	5015.829

Figure 19 Typical chromatogram of a control apple juice sample. Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II. The sample contained <0.05 ppm equivalents of BAS 300 I.

[93186] 2 B9318611,3,1
Reported on 20-DEC-1993 at 15:02

Acquired on 18-DEC-1993 at 12:50



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : CONTROL A. JUICE
Sample Id : 9304206
Sample Type : Control Amount=1.00000
Bottle No : 3

PEAK INFORMATION

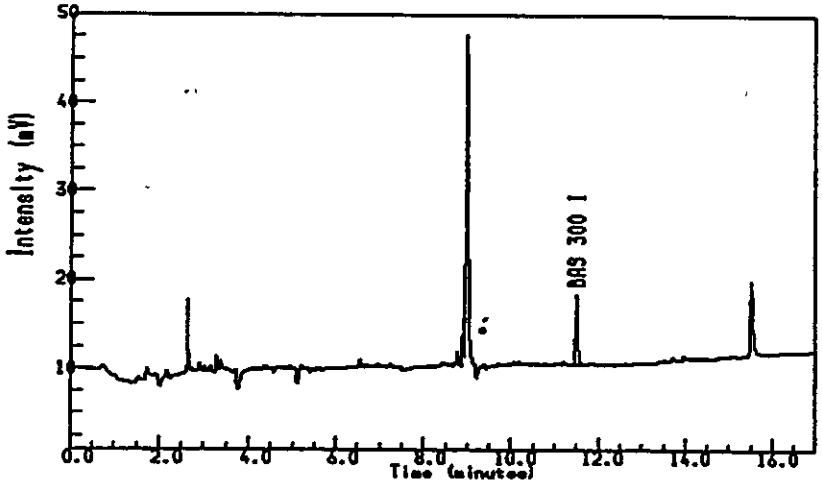
RT mins	Hght uV	ppb	Peak name

Totals		
Unknowns	0	N/A
	0	0.000
	0	0.000

Figure 20 Typical chromatogram of a control apple juice sample fortified with 0.05 ppm of BAS 300 I (the quantitation limit). Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

[93186] 2 B9318611,9,1
Reported on 20-DEC-1993 at 15:02
DSM

Acquired on 18-DEC-1993 at 15:16



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 0.05 PPM A
Sample Id : 9304206
Sample Type : Recovery Amount=1.00000
Bottle No : 6

PEAK INFORMATION

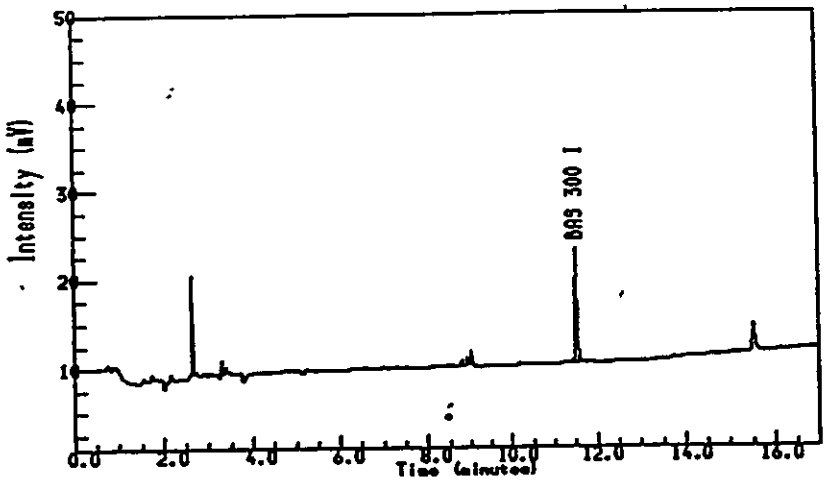
RT mins	Hght uV	ppb	Peak name
11.499	7851	50.631	BAS 300 I

Totals		
Unknowns	0	N/A
	7851	50.631
	7851	50.631

Figure 21 Typical chromatogram of a control apple juice sample fortified with 0.50 ppm of BAS 300 I. Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

[93186] 2 B9318611,18,1
Reported on 20-DEC-1993 at 15:03
DSM

Acquired on 18-DEC-1993 at 18:55



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 0.50 PPM A
Sample Id : 9304206
Sample Type : Recovery Amount=1.00000
Bottle No : 13

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
11.515	12959	453.556	BAS 300 I

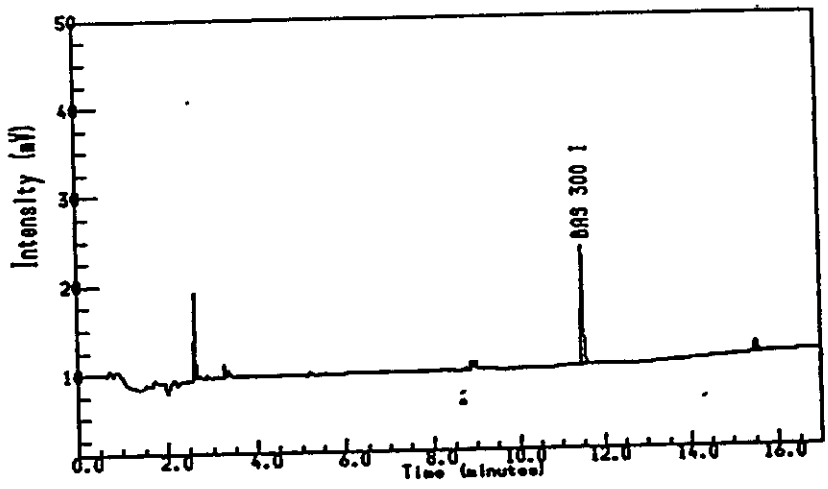
Totals		
Unknowns	0	N/A
	12959	453.556
	12959	453.556

Figure 22 Typical chromatogram of a control apple juice sample fortified with 5.0 ppm of BAS 300 I. Sample number 9304206 from master sheet number 9318611. Data for this sample can be found in Table II.

[93186] 2 B9318611,26,1
Reported on 20-DEC-1993 at 15:04

DSM

Acquired on 18-DEC-1993 at 22:10



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY
Lims Id :
Comment :
Method Title :
Sample Name : 5.0 PPM B
Sample Id : 9304206
Sample Type : Recovery Amount=1.00000
Bottle No : 18

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
11.493	13347	4694.007	BAS 300 I
15.515	1403	0.000	
Totals			
Unknowns	0	N/A	
	14749	4694.007	
	14749	4694.007	